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Spray Combustion Studies of Surrogate Hazardous Waste Incineration

California Univ., Davis

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16. ABSTRACT

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementation, and management of research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

(Then follows a paragraph relating the publication in hand to one of the solution groups listed above.)

E. Timothy Oppelt, Acting Director
Risk Reduction Engineering Laboratory

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ABSTRACT

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The relative order of DE from most to least difficult to destroy was determined to be 1,2,4-trichlorobenzene > tetrachloroethene > trichloroethene > 1,1,2,2-tetrachloroethane > 1-chloropentane > heptane. The order is as predicted by thermal stability ($TSLoO_2$) or theoretical flame mode kinetics (TFMK) under low oxygen conditions. This was true even though about 20% excess combustion air was supplied. Increased emissions of carbon monoxide (CO) were noted when burning the 5.3% by weight chlorine-containing mixtures. Some evidence for a relationship between CO and benzene emission was observed for the specific conditions tested. Based in part upon results of single droplet studies and chlorine combustion chemistry, it was hypothesized that the relationship resulted from the H-atom scavenging properties of chlorine species such as HCl and Cl.

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This study was made possible with the assistance of a Cooperative Research Agreement #CR-813333-01 which supported one author (Chang) during a sabbatic leave from the University of California, Davis. For that opportunity he is grateful to both the U.S. Environmental Protection Agency and the University of California. The California Air Resources Board supported the effort that was carried out at the University of California, Davis under contract #A6-051-32.

ACRONYMS

BZ	Benzene
CARB	California Air Resources Board
CARB TET	Carbon Tetrachloride
CHC	Chlorinated Hydrocarbon
CHL	Center Hill Laboratory
CD	Chlorodecane
ClBZ	Chlorobenzene
CP	Chloropentane
DCM	Dichloromethane
DE	Destruction Efficiency
EDC	Ethylene dichloride
EERC	Energy and Environmental Research Corporation
EMSL	Environmental Monitoring and Support Laboratory
EPA	Environmental Protection Agency
FID	Flame Ionization Detector
F113	Freon 113
FTA	Fraction Theoretical Air
GC	Gas Chromatograph
$GPTSLoO_2$	Gas Phase Thermal Stability Ranking for Low Oxygen
Hc	Heat of Combustion
HC	Hydrocarbon
HWI	Hazardous Waste Incineration
MS	Mass Spectrometry
PERC	Perchloroethylene (tetrachlorethene)
PIC	Product of Incomplete Combustion in Appendix VIII
POHC	Principal Organic Hazardous Constituent
Pt	Penetration (1 - DE)
QA	Quality Assurance
QC	Quality Control
ROSE	Residual Organic Substance Emission
SOP	Statement of Procedure
SVO	Semi-volatile Organic Compound
TAC	TENAX/Ambersorb/Charcoal
TC	Thermocouple
TCA	Trichloroethane
TCB	Trichlorobenzene
TCE	Trichloroethene
TECA	Tetrachloroethane
TFMK	Theoretical Flame Mode Kinetics
TFR	Turbulent Flame Reactor
TOL	Toluene
$TSHiO_2$	Thermal Stability High Oxygen Conditions
$TSLoO_2$	Thermal Stability Low Oxygen Conditions
UCD	University of California, Davis
UDRI	University of Dayton Research Institute
VOC	Volatile Organic Compound

SPRAY COMBUSTION STUDIES OF SURROGATE HAZARDOUS WASTE INCINERATION

INTRODUCTION

This research project had its origins in a study at the University of California, Davis (UCD), under the sponsorship of the California Air Resources Board (CARB). An investigation of the burning characteristics of individual droplets of chlorinated hydrocarbon (CHC) and hydrocarbon (HC) fuel mixtures was targeted at determining whether individual droplet burning-rates or flame extinction characteristics could be used to develop a flame-based "incinerability ranking scale." Such a scale would complement a promising existing ranking scale based upon post-flame thermal decomposition kinetics (Dellinger et al., 1985a).

Waste incineration was conceptualized as a two-stage process, illustrated in Figure 1: a flame-zone where very high temperatures (near adiabatic), extremely rapid reactions, and high concentrations of reactive species characteristic of flames, converted chemicals introduced with the fuel/waste mixture on relatively short time scales (< 0.1 second); and a second high temperature thermal decomposition zone characterized by slower reaction rates, lower concentrations of reactive species, but having longer residence time ($\approx$ 1 second) so that appreciable conversion of reactants could persist. In such a model, destruction efficiencies (DE) of from 90 to 99% are expected in the flame-zone (Clark et al., 1985; Wolbach and Garman, 1985). A possible explanation for the escape of some reactants can be described by the "rogue droplet" hypothesis, in which an oversize particle of fuel/waste passes out of the flame-zone before completing evaporation (Clark et al., 1985; Mulholland, 1987). In such a circumstance, the oversize droplet could behave as an isolated burning droplet. It is known that individual droplets which have been ignited and which sustain a flame will eventually extinguish before complete consumption of the reactants. "Droplet extinction" is the term which has been applied to the phenomenon and a physico-chemical explanation has been given by Law (1975). In such a case, only one out of multitude of droplets need escape the flame to account for levels of residual organic substances (ROSE) commonly observed at low levels in

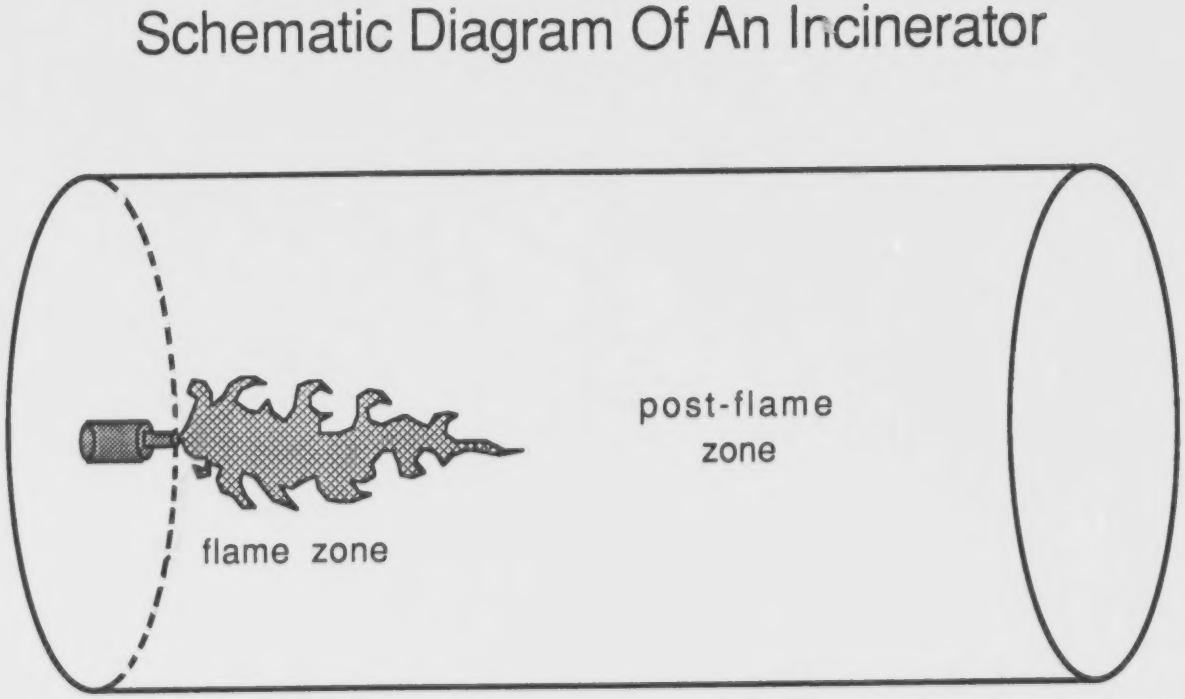

Figure 1. Schematic diagram of an incinerator illustrating two combustion zones

incinerators.[1] Therefore, a goal of the UCD study was to determine whether physico-chemical properties of a particular chemical compound would also affect burning-rates and droplet extinction, thereby altering the relative amounts of wastes which might escape the flame-zone.

If the conceptual models described above should prove to be reasonably accurate, then a flame-based ranking scale (either based on burning-rate or droplet extinction diameter) could be developed to complement the University of Dayton Research Institute (UDRI) gas-phase thermal stability (GPTS) ranking. The logic would be that those compounds highly ranked on both scales would be difficult to destroy in liquid-injection incinerators. Therefore they would be suitable candidates for surrogate compounds to be used in testing the ability of an incinerator to destroy the principal hazardous organic constituents (POHC) of a waste. The UCD study dealt only with single droplet burning, whereas in liquid-injection incineration, combustion most often occurs in turbulent diffusion flames. Typically, liquid sprays are generated, and burning occurs at the periphery of evaporating clouds of droplets because of rate limitations on the mixing of oxidant into the cloud. A major question to be addressed as part of the current project was whether any of the single droplet results could be related to spray-combustion results when oversize droplets, a simulated "failure-mode", were purposely introduced into a turbulent diffusion flame. The existing turbulent flame reactor (TFR) at the U.S. Environmental Protection Agency's (EPA) Center Hill Laboratory (CHL) was the setting of choice at which to conduct the experiments and was the reason for undertaking this cooperative research program with UCD.

This report deals with an experimental study of oversized droplets burning in a TFR and concommitant development of sampling and analytical methods in support of those experiments.

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1 The term residual organic substance emission (ROSE) is being used in this report to refer to those organic compounds which are in the feed, e.g. POHCs, but not completely destroyed by the combustion process, those compounds which are possibly reformed or newly formed in the incinerator (not limited to the USEPA definition of product of incomplete combustion, PIC, which requires appearance in "Appendix VIII"), and those compounds which represent products other than inorganic combustion products such as CO, CO_2, H_2O, HCl, or Cl_2.

BACKGROUND

In typical hazardous waste incinerators (HWI), the residence time in the hot post-flame zone is sufficiently long to complete combustion. An investigation performed by the University of Dayton Research Institute (UDRI) has shown that the correlation between POHC incinerability ranking scales and actual field measurements of DE was best with a ranking based upon gas-phase thermal stability ($GPTSLo_{O_2}$) under low oxygen conditions (Dellinger, et al., 1985a). The rationale provided for using a ranking based upon thermal stability (a non-flame experimentally based test) was that the concentration of POHCs exiting the flame-zone would be in the same proportions as was originally present in the waste, hence destruction efficiency (DE) in the post-flame zone would govern the fraction of POHCs remaining. A reasonable question to ask is, "Do relative POHC concentrations differ exiting the flame-zone?" and, "Does this occur for 'rogue droplets'?"

To address the above questions, it is worthwhile to discuss the "gasification" (vaporization and burning) of droplets. The gasification of droplets has been studied extensively over the past thirty years. As a result there exists an understanding of how droplets are gasified in both oxidizing and pyrolytic (oxygen absent) environments. A schematic diagram of a burning droplet is presented in Figure 2. In a steady-burning mode, a liquid droplet is surrounded by a) an inner zone, containing vaporized fuel, pyrolysis and combustion products, b) a thin flame region, which is a source of heat and combustion products, and a sink for fuel and oxygen, and c) the surrounding air which is the source of oxygen for combustion reactions. It is apparent that the fuel and oxygen are separated by the flame. Because the fuel and oxygen must be transported by diffusion to the flame region for a reaction to take place, the flame surrounding a liquid droplet is a diffusion flame (referred to as a "flamelet" in this report). The fuel and oxidizer combine in the flame or reaction region. In contrast, the fuel and oxidizer in premixed flames are already in intimate contact prior to reaching the reaction zone. The thickness of both diffusion and premixed flames is governed by the rate of chemical reaction; high rates of reaction result in thin flames and low rates of reaction lead to thicker flames.

As an isolated droplet gasifies, measurements of its dimensions can be made. A typical gasification profile is shown in Figure 3. It consists of a transient region of initial heating and ignition of the droplet, a region of steady-burning, and an abrupt change to a new gasification rate corresponding to pure vaporization (no burning). In the steady-burning droplet profile, the gasification rate is diffusion-limited, i.e., it is essentially independent of the chemical reaction rate occurring in the reaction zone. However, as the droplet becomes smaller, the rate of diffusion of heat and mass away from the droplet increases relative to the chemical reaction rate. At some critical diameter, the chemical reaction rate can no longer

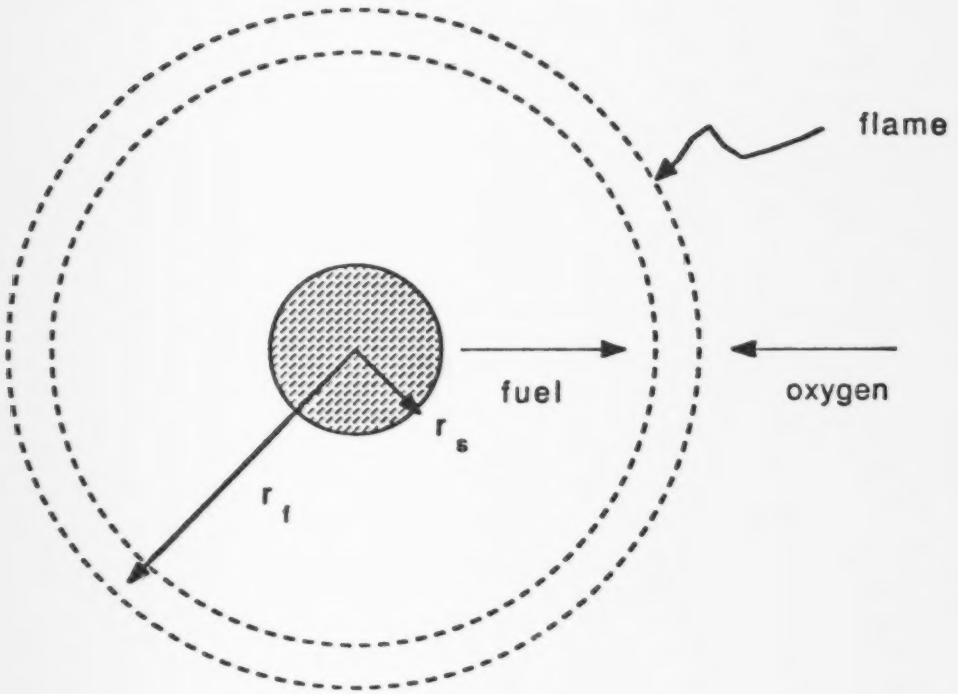

Figure 2. Schematic of burning droplet, r_s = droplet radius, r_f = flame radius

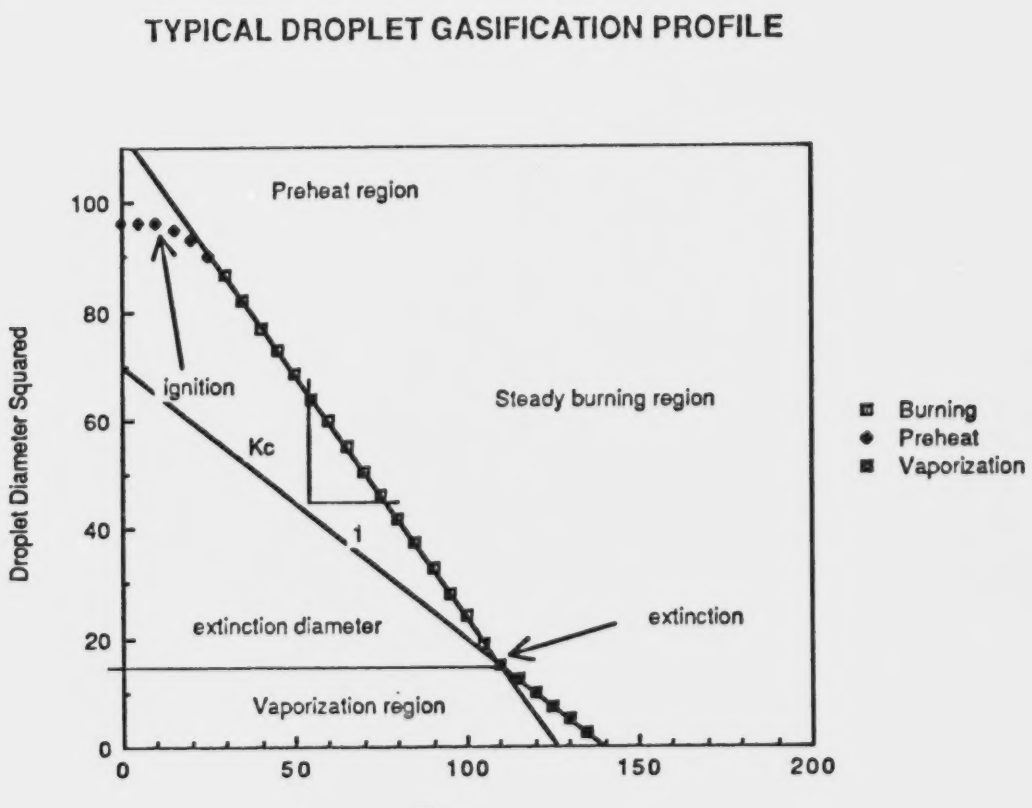

Figure 3. Gasification profile of a typical burning droplet.

supply heat fast enough to keep up with the increased diffusion rate. Thus some of the reactants are not fully converted to products of complete combustion, resulting in reactant "leakage" through the flame and a drop in flame temperature. Typically, reaction rates have a strong dependence upon temperature, as can be seen from an Arrhenius form of the rate constant for an elementary reaction:

$$k_r \approx A*\exp\{-E_a/(RT)\},$$

where A is a pre-exponential factor related to the rate of collisions, E_a is the activation energy of the reaction, R is the gas constant, T is absolute temperature and k_r is the rate constant. It can be seen that a small decrease in T results in a large decrease in k_r whenever the product RT E_a. As a result of this process, at some finite diameter, the flame around the droplet is extinguished. Therefore the "extinction diameter" represents the droplet diameter at which a flame can no longer exist around a droplet. The droplet extinction diameter is important because after that point, gasified fuel molecules no longer pass through the hot reaction zone of a flame; they are simply vaporized.

A consequence of flame extinction is that a fraction of the fuel/waste mixture is not passed through a flame. Instead it must be thermally degraded during the residence time in a relative cooler environment. Measurements of composition of the droplets at various points in the gasification profile can reveal whether significant enrichment of one liquid component relative to another can occur during a droplet's lifetime. Measurements of burning profile and droplet composition were goals of the study underway at UC Davis.

The relationship between burning of isolated droplets and droplets in sprays is not clear-cut. There has been considerable discussion over the past decade on the role of group-burning versus individual droplet burning. The ratio of inter-drop distance to drop diameter, C, has been found to be an important parameter which governs whether a spray burns as a group or as individual droplets. For droplets far apart ($C > 10$) individual droplet behavior is expected. For very dense sprays ($1 < C < 5$), there are intense interaction effects between droplets. However, for most sprays ($C = 10$) single droplet vaporization theory still applies (Correa and Sichel, 1982). Thus single droplet burning can be used to describe spray combustion when droplets are far apart, and droplet vaporization effects can be used to describe vaporization which occurs in the spray interior. In the current study, it was hoped that it would be possible to relate the results of the single droplet experiments to those of sprays, thereby gaining insight into the importance of various mechanisms.

EXPERIMENTAL METHODS

In order to sample for the semi-volatile organic compounds (SVO) in use in the UC Davis study, it was first necessary to modify the existing sampling procedure in use at the CHL. That method involved use of an Envirochem^{R} UNACON 810 thermal desorption unit to desorb samples collected on TENAX-TA^{R} packed into tubular Pyrex^{R} traps. For reasons of equipment costs, data comparability and physical limitations imposed by the desorption unit involved, it was desirable that the same quartz tubes serve as the housing for whatever sorbent materials were used in the study. Two additional constraining problems had to be overcome: one was the transmission of higher boiling compounds down the sampling line, and the second was the avoidance of water vapor condensation in the sorbent traps. These problems were overcome by maintaining the sampling line and a commercially available multi-sorbent trap at higher temperatures (150 to 160 ^{o}C and 74 ^{o}C, respectively) than the typical VOST or modified VOST trains. A preliminary validation of the sampling method was undertaken for purposes of this research project. It was felt that if the method showed promise, then further method validation might be undertaken by a sister laboratory (EMSL).

Sampling System

The sampling system used in the study is shown in Figure 4. It consisted of the following items:

a) A 6 mm o.d. quartz probe tip into which a plug of glass wool was inserted.

b) A Teflon/stainless steel sample line isolation valve.

c) Stainless steel "tees" for standard spike injection or nitrogen purge.

d) A heated, temperature-controlled 6.35 mm (1/4 in.). o.d. stainless steel tube sampling line 150 to 160 ^{o}C.

e) A heated, temperature-controlled (74 ^{o}C) aluminum block which contained the sorbent trap.

f) An Envirochem^{R} TENAX-TA/Ambersorb/Charcoal (TAC) sorbent tube, 204 mm long X 6 mm o.d. X 4 mm i.d.

g) A rotameter equipped with a needle valve for flow control

h) A vacuum gauge.

i) A silica gel drying column.

j) An airtight sample pump.

k) A one liter per revolution dry gas meter.

DIAGRAM of TAC SAMPLING LINE for VOC & SVOCs

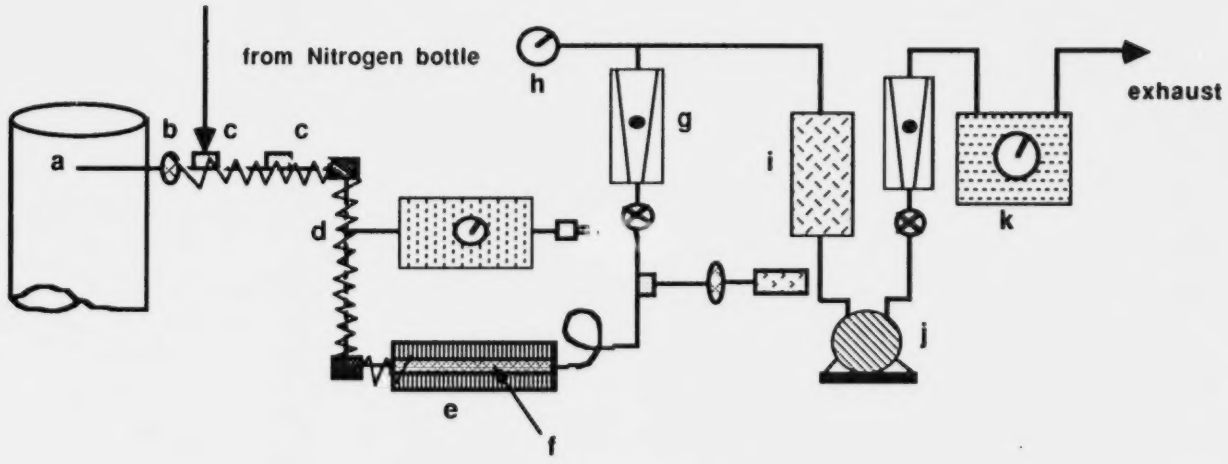

Figure 4. TAC Sampling System. (a) 6 mm o.d. quartz probe tip into which a plug of glass wool was inserted; (b) Teflon/stainless steel sample line isolation valve; (c) stainless steel "tees" for standard spike injection or nitrogen purge; (d) heated, temperature-controlled 6.35 mm (1/4 in.). o.d. stainless steel tube sampling line 150 to 160 °C; (e) heated, temperature-controlled (74°C) aluminum block which contained the sorbent trap; (f) Envirochem (TAC) sorbent tube, 204 mm long x 6 mm o.d. x 4 mm i.d.; (g) rotameter equipped with a needle valve for flow control; (h) vacuum gauge; (i) silica gel drying column; (j) airtight sample pump; (k) one liter per revolution dry gas meter.

The retention efficiency of a standard mixture was determined by first "spiking" the TAC tubes with the compounds and drawing combustion gas through the tubes. A test of sampling efficiency was performed by injecting a standard mixture at the head of the sampling line while drawing combustion gases through the line and sorbent tube. For this study two liters of TFR combustion gas were drawn through the multi-sorbent tubes at an approximate rate of 200 ml/minute. Between samples, the sampling line was purged with nitrogen (> 5 liters). Analyses of the sorbent tubes and standards were carried out using the standard operating procedures described in the section on Analytical Methods (see below).

Conventional Gas Analyzers

The existing gas sampling train was used to measure carbon dioxide (CO_2), carbon monoxide (CO) and oxygen (O_2) concentrations in the combustion gases. A gas scrubber containing 0.1 N H_3PO_4/NaH_2PO_4 solution was added to the sampling train to remove hydrogen chloride (HCl) before it reached the analyzers. A hydrocarbon analyzer was inoperative throughout the duration of the testing, consequently total unburned hydrocarbons were not measured. A schematic diagram of the sampling train is shown in Figure 5. Gas analyzers were calibrated with zero and span gases daily before each run.

Analytical Methods

The primary purpose of the oversize droplet experiments was to determine relative compound DE of simple mixtures of chlorinated hydrocarbons (CHC). Determination of the identity of ROSEs was a secondary goal of this study. For that reason and because of the greater reliability of the flame ionization detector (FID), it was decided that the samples would be analyzed by GC/FID. A mass spectrometer (MS) analysis was performed on two samples for the specific purpose of identifying some recurring ROSEs. Two identically configured GCs were utilized so that compounds identified with the MS could be correlated with peaks determined with the FID unit. The correlation is shown in Figure 6 where data from both units have been compared. In order to use the linear regression obtained, the GC/FID retention time of a given sample would need to be corrected so that the retention time of the internal standard, bromofluorobenzene (BFB), was the same as that used in the preparation of the correlation, i.e., 1278 s. (See Table 1.) The analytical conditions for both GCs were as follows:

a) Sample introduction: Envirochem^R UNACON 810A concentrating capillary inletting accessory/thermal desorption unit.

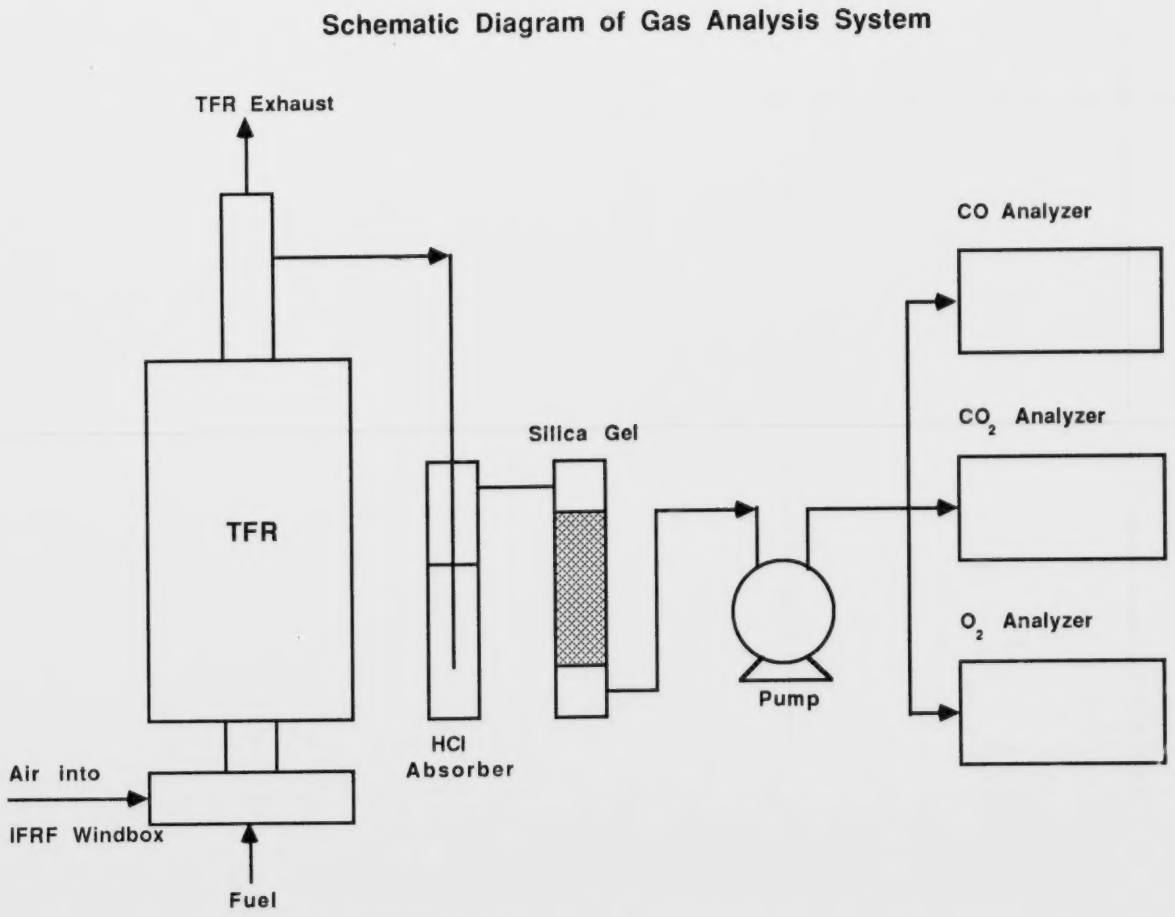

Figure 5. Schematic diagram of continuous analyzer gas sampling system.

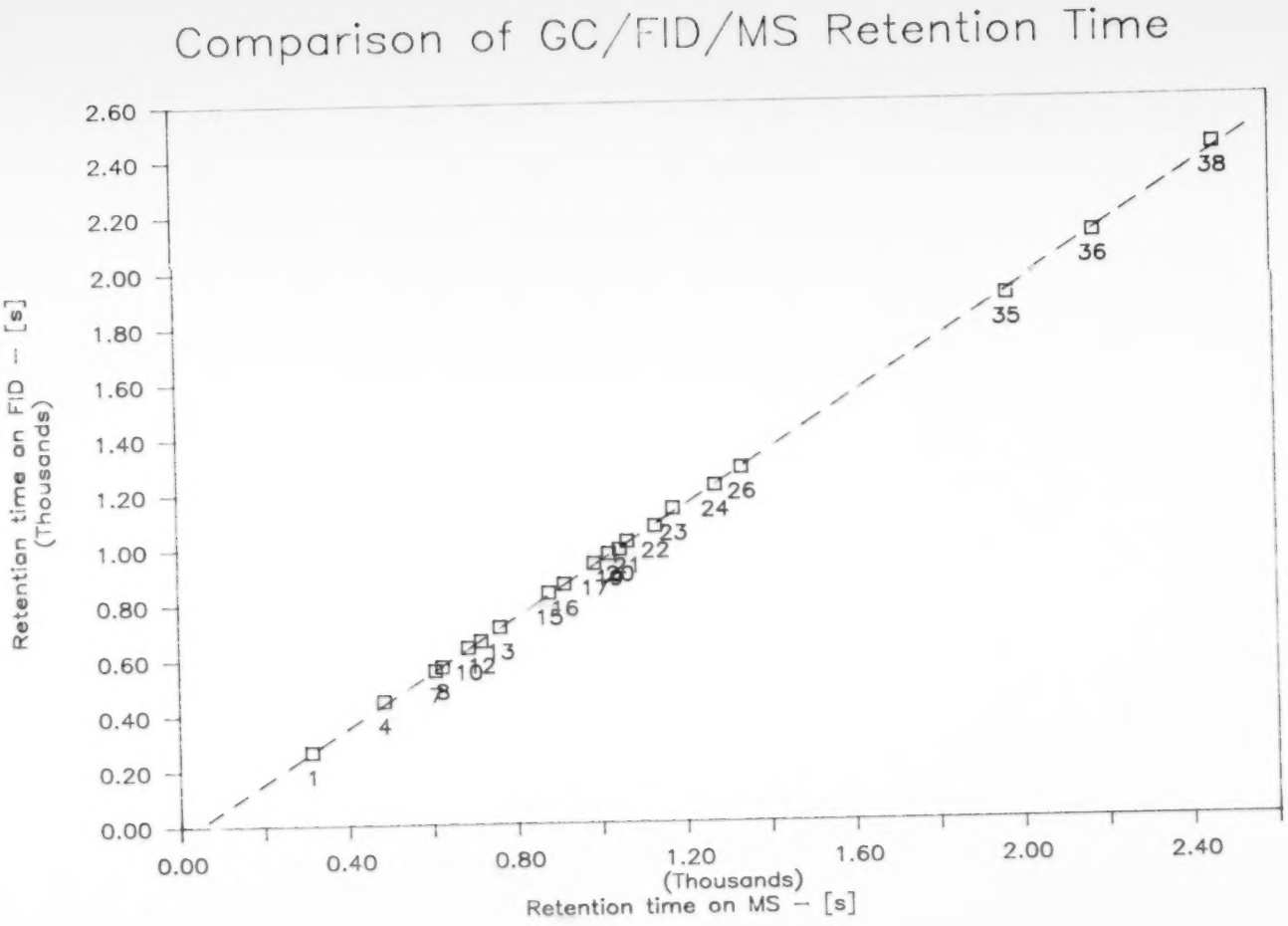

Figure 6. Comparison of GC/FID/MS retention times corrected for BFB retention time.

Table 1

Boiling Point and Retention Times

Compound	B.P. [°C]	Combined data MS [s]	FID [s]	Label
DCM	40.5	313	265	1
F113	47.7	330		2
1-hexene	63.4	452		3
chloroform	61.2	485	447	4
1,2-dichloroethane	84.0	546		5
1-chlorobutane	78.4	577		6
BZ	80.1	608	557	7
CARB TET	76.8	624	569	8
2-methylhexane	90.0	668		9
pentanal	103.0	686	639	10
3-methylhexane	92.0	692		11
TCE	87.0	717	662	12
HEPT	98.4	762	712	13
methylcyclohexane	100.4	816		14
1-chloropentane		879	832	15
TOL	110.6	916	863	16
hexanal	128.0	987	937	17
3-methyleneheptane		1017		18
4-octene?	122.0	1022	971	19
PERC	121.0	1048	986	20
4-octene?	122.0	1066	1015	21
ClBZ	132.0	1132	1069	22
1-chlorohexane	134.5	1175	1132	23
TECA	146.0	1275	1215	24
nonane	150.8	1337		25
BFB	152.0	1338	1278	26
benzaldehyde	178.1	1410		27
benzofuran	174.0	1534		28
1,4-dichlorobenzene	174.0	1559		29
nonanol	212.0	1565		30
1,2-dichlorobenzene	179.0	1572		31
1-decene	170.6	1588		32
1-chlorononane	203.0	1713		33
3,7-dimethyloctanol	212.0	1808		34
1,2,4-TCB	231.5	1973	1895	35
1-chlorodecane	223.4	2185	2110	36
1-bromodecane	240.6	2349		37
tetradecane	253.7	2470	2422	38
5,7-dimethylundecane		2832		39
2,3,6-trimethyldecane		2833		40

b) Instruments: Hewlett-Packard 5880A GC/FID or Finnegan 4023 GC/MS.

c) Columns: J & W Scientific, DB-1, 30 m X 0.32 mm i.d., fused silica capillary column. Stationary phase cross-linked and bonded.

d) Carrier gas: Helium at 2 cc/min.

e) Column temperature program: 4 min. at 10 °C ramped to 220 °C at 4 °C/min and held for 2 min.

f) Standards Sources: USEPA Repository for Toxic and Hazardous Materials or Aldrich Chemical Company, Inc. (highest purity available).

Quality control (QC), quality assurance (QA) plans had previously been prepared for the CHL and a standard operating procedure (SOP) for the analysis was available. A copy of the SOP has been appended to this report in Appendix A. The experiments reported herein were considered to be range-finding and not in support of regulatory actions. Therefore they were subject to Category 4 QA/QC procedures.

The internal standard BFB and the standards used to "spike" the sorbent tubes were delivered to the sorbent tubes from methanol solution. Unfortunately the additional sorbents present in the TAC tubes (activated carbon and Ambersorb) retained methanol whereas TENAX-TA alone allowed the solvent to pass through with little retention. As a result a large solvent peak would occur which often masked those compounds eluting with retention times less than about 8 minutes. Consequently, the Envirochem thermal desorption unit was used in a nominally 10:1 sample split mode to desorb the majority of the sample onto a TENAX-TA tube (sample saver option of UNACON 810A). A smaller portion of the sample was desorbed directly into the GC for analysis. The TENAX-TA tube could subsequently be analyzed for quantitation of peaks. A fixed proportion of the sample (95 ± 2%) was determined to have been delivered from the sorbent tube to the GC. This was accomplished by comparing the areas of those peaks not masked by the methanol solvent peak in two successive analyses.

The data acquisition system of the gas chromatograph was set up to quantify and "identify" peaks on the basis of relative retention times in comparison with the BFB internal standard. Occasionally it was observed that a peak assignment by the data acquisition system's built in algorithm was incorrect. Usually this was because of an interfering compound in the combustion effluent eluting with a similar retention time, so that peaks were either very closely spaced or incompletely resolved. In such cases chromatograms were individually examined and the relative spacings between "known" peaks were used to aid in the identification process. This was particularly true for carbon tetrachloride and benzene. In fact, because benzene was generated in

relatively large quantities under poor atomization conditions, no attempt was made to study the DE of carbon tetrachloride.

Identification of ROSEs

The identification and quantification of all chromatographic peaks were not attempted as part of this study. Also, searches for molecular ions less than 33 amu were avoided so that the number of low molecular weight compounds identified was limited. Rather, selected peaks corresponding to anticipated products of incomplete combustion (PIC) were sought out. Compounds were first compared against the Finnegan-supplied GC/MS library. The library search produced proposed matches which were further evaluated for purity and goodness of fit of the mass spectrum. A summary of some selected compounds tentatively identified is shown in Table 1 along with the retention time on the GC/MS and the compound's boiling point. A plot of compound boiling point and retention time (shown in Figure 7) was used to assist with the detection of unreasonable library matches.

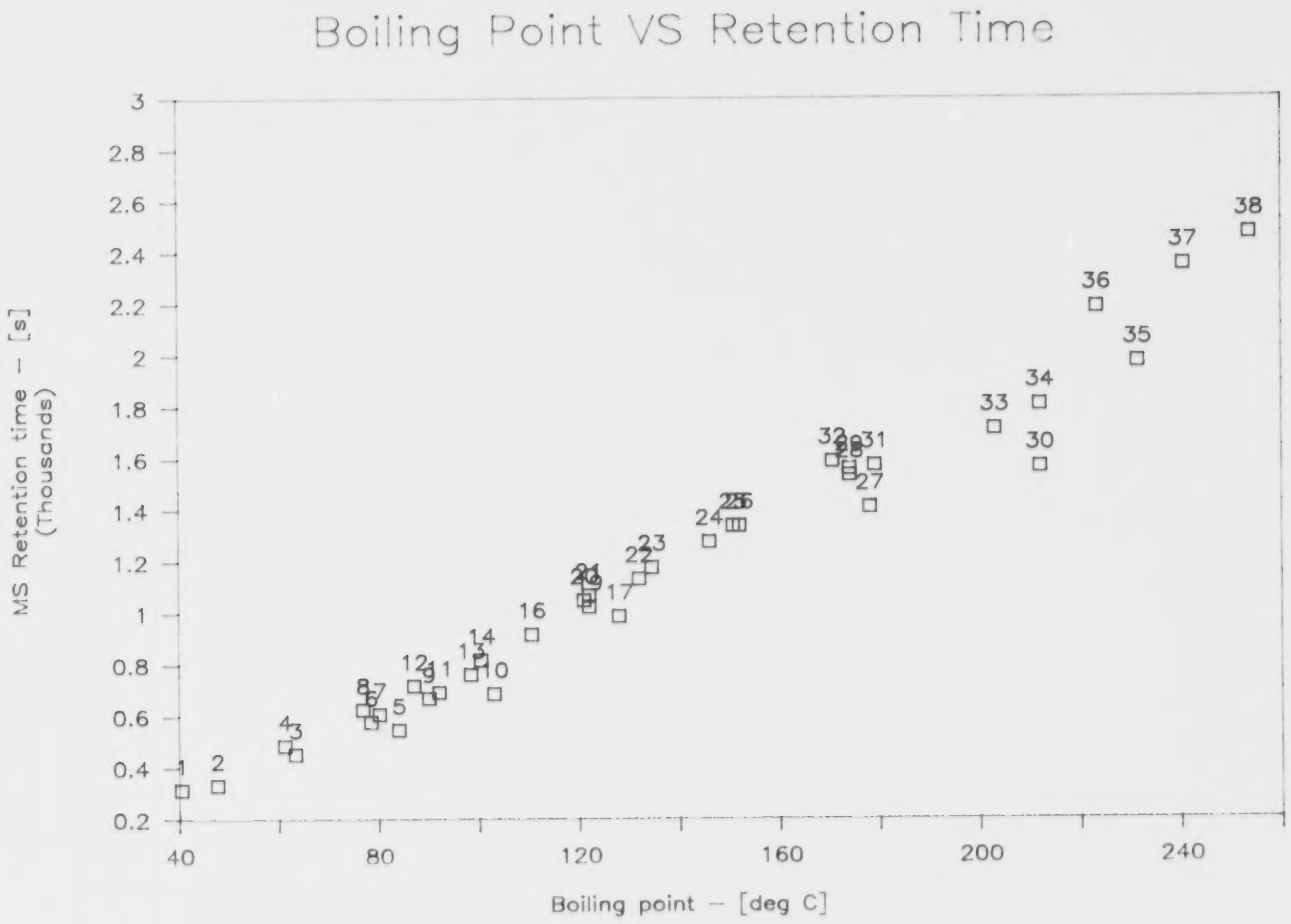

Figure 7. Compound boiling point versus retention time - used to verify tentative MS compound identifications.

RESULTS OF TAC SORBENT TUBE RETENTION AND RECOVERY STUDY

The retention of candidate POHC compounds on the TAC tubes was determined for the sampling train conditions described above. Known amounts of standards were delivered from solution to the glass frit at the inlets of the tubes and evaporated into a stream of helium drawn through the tubes. A triplicate set of tubes was exposed to two liters of combustion gases from the TFR while technical grade heptane (HEPT) was being burned. The tubes were subsequently analyzed for the amount of each POHC remaining in comparison to identically "spiked" tubes which had not been exposed. It was assumed that the BFB recovery was 100% in each case, and the results of the other compound recoveries was normalized to the amount of BFB recovered. The results are shown in Table 2 (column labelled "retention efficiency"). The results clearly indicate that considerable loss of dichloromethane, carbon tetrachloride, and trichloroethene occurred at the 74 ^{o}C test condition. Furthermore, a higher degree of sample variability was also observed for these compounds. Nevertheless, the TAC tubes did demonstrate an ability to retain a fraction of the lower molecular weight compounds, so that a qualitative statement could be made with regard to their presence in the sampled gas even though a quantitative estimate would be subject to large uncertainties.

The results of "spiking" known quantities of the standards from solution at the head of the sampling line are also shown in Table 2 (column labelled "recovery efficiency"). In this case the "spike" was evaporated into two liters of TFR combustion gas which was passed through the TAC sorbent tube. Slightly higher recoveries of the "spiked" compounds was noted. This can probably be attributed to the lower total amount of gas passed through the sorbent tube, and in the case of heptane, to residual amounts of heptane in the TFR gas. In the oversized droplet POHC DE studies described below, DEs were corrected for recovery efficiencies shown in Table 2.

The above assessment of the TAC tubes and sampling line indicated that while operation at elevated temperatures ensured transmission of the POHCs of interest (SVOs) and prevention of water vapor/HCl condensation, recovery of volatile organic compounds (VOC) normally trapped by the VOST methodology was less than desired. However, the multi-sorbent tubes extended the range of compounds that could be successfully captured on a single trap to both VOCs and some SVOs, and could be used for qualitative study of the VOCs.

Table 2

Retention and Recovery Efficiency Results

Standard	Retention efficiency	std. dev.	Recovery efficiency	std. dev.
DCM	19%	13%	27%	14%
CC14	54%	9%	125%*	24%
TCE	41%	15%	50%	13%
HEPT	107%	17%	116%	10%
CP	107%	16%	112%	9%
PERC	65%	19%	71%	9%
CLBZ	103%	16%	105%	8%
TECA	79%	16%	82%	6%
TCB	105%	20%	91%	16%
BFB	100%	n.a.	100%	n.a.

*benzene interference
n.a. = not applicable

OVERSIZE DROPLET MIXTURE SELECTION

Selection of the pairs of POHCs to be burned with the heptane (HEPT) was based upon several considerations. First, since the results were to be compared with single dropletburning studies at UC Davis, it was necessary to limit the compounds to those that had boiling points greater than about 90 ^{o}C. This essentially eliminated compounds such as dichloromethane (DCM), Freon 113 (F113), and chloroform. For comparability with previous testing on the TFR, and to select compounds known to be difficult to destroy, trichloroethene (TCE), 1,1,2,2-tetrachloroethane (TECA), and tetrachloroethene (PERC) were selected. In addition, recent work had shown that 1,2,4-trichlorobenzene (TCB) might be difficult to destroy both in flame and non-flame environments (Chang, 1986; Dellinger, 1985b). Compounds initially studied at UC Davis included 1-chloropentane (CP) and 1-chlorodecane (CD). Unfortunately, the TAC tube studies revealed difficulties with the analysis for CD, leaving only CP to be tested. Thus the five compounds CP, TECA, TCE, PERC and TCB were selected for the initial study. They provided a range of difficulty in anticipated incinerability. A second consideration regarding the pairs of compounds to burn centered around the anticipated ROSEs to be formed. It would be undesirable for a primary decomposition product to also be one of the POHCs selected, therefore, mixtures of TECA with TCE were avoided since TCE was a known decomposition product of TECA. Finally, to reduce the variability in stoichiometry, it was decided to concoct the mixtures such that equimolar amounts of each POHC would be blended with heptane to yield an overall H:Cl ratio of 100:1 (about 5.3 weight % Cl). The composition of the "cocktails" is shown in Table 3.

Previous work with the TFR (Kramlich et al., 1985) had demonstrated that oversize droplets could be produced by simply reducing the pressure supplied to the atomizing nozzle. In order to maintain the thermal environment in the TFR as close to the same as possible, identical fuel feed rate, stoichiometry and turbulent mixing (swirl setting) were used. One physical difference in the spray pattern from Kramlich et al.'s earlier study was the use of a slightly smaller cone angle on the nozzle to reduce the possibility of direct impact of large droplets on the cooled walls of the TFR. Thus a 1.5 gph, WDA 60^{o} hollow-cone nozzle operated at 40 psig was used to produce the oversized droplets, whereas a 1.0 gph, WDA 90^{o} hollow-cone nozzle operated at 120 psig was used for nominally "optimum" droplet atomization. No measurements were made of droplet size distribution, however, it was evident from the flame pattern (much longer and lazier in appearance) and from observation of the spray during cold fuel flowrate measurements that considerably larger droplets were present. The conditions for the tests are summarized in Table 4.

Table 3

POHC Properties and Mixture Compositions

Compound	m.p. [°C]	b.p. [°C]	density [g/ml]	M.W.	C atoms per mole	H atoms per mole	Cl atoms per mole
CP	-99.0	107.8	0.882	106.6	5	11	1
1,1,2,2-TECA	-36.0	146.0	1.590	167.9	2	2	4
1,2,4-TCB	17.0	231.5	1.454	181.5	6	3	3
PERC	-19.0	121.0	1.623	165.8	2	0	4
TCE	-73.0	87.0	1.464	131.4	2	1	3
HEPT	-90.6	98.4	0.684	100.2	7	16	0

Mixture	average composition C	H	Cl	Cl conc. wt. %
CP:TECA:HEPT	1.00	2.27	0.023	5.3%
TECA:TCB:HEPT	1.00	2.24	0.022	5.3%
PERC:TCB:HEPT	1.00	2.24	0.022	5.3%
TCE:TCB:HEPT	1.00	2.23	0.022	5.3%

CP chloropentane
PERC tetrachloroethene
TECA tetrachloroethane
TCB trichlorobenzene
TCE trichloroethene
HEPT heptane (technical grade)

Table 4

Summary of Test Conditions Oversize Drop Study

Test Mix	Pressure [psig]	Fuel Flow [ml/s]	FTA	CO @ 0% O2 [ppm]	Swirl	Temp [°C]
HEPT	40	0.92	1.22	702	1.1	
CP:TECA:HEPT	40	0.92	1.27	969	1.1	489
HEPT	40	0.92	1.22	426	1.1	
TECA:TCB:HEPT	40	0.92	1.26	886	1.1	482
HEPT	40	0.91	1.22	405	1.1	
PERC:TCB:HEPT	40	0.91	1.25	787	1.1	504
HEPT	40	0.93	1.26	582	1.1	
TCE:TCB:HEPT	40	0.93	1.26	875	1.0	476
HEPT*	120	0.99	1.18	27	1.1	
TCE:TCB:HEPT*	120	0.99	1.20	40	1.1	507

*Optimum atomization pressure

OVERSIZE DROPLET RESULTS AND DISCUSSION

Clear differences in the DE of the fuel/POHC cocktails were observed. The differences were smaller for the most refractory compounds TCB and PERC, but were several orders-of-magnitude between the most and least refractory POHCs tested, TCB and CP, respectively. A relative ranking of compounds was constructed from the observed absolute penetrations (Pt = 1 - DE). This was accomplished by normalizing to a common compound between pairs and assuming a TCB penetration of unity. No physical significance should be attached to the numerical values of the relative Pt reported. The ranking is shown in Table 5 along with a ranking based on heat-of-combustion (Hc), gas phase thermal stability high O_2 ($TSHiO_2$), low O_2 ($TSLoO_2$), and theoretical flame mode kinetics (TFMK). The actual DEs observed for one control test (TCE:TCB:HEPT) with nominally optimum droplet atomization and for oversize droplets are also shown for comparison in Table 6.

As has been demonstrated in other studies, Hc and $TSHiO_2$ would be relatively poor predictors of compound incinerability. On the other hand, the observed results are consistent with predictions of either $TSLoO_2$ or TFMK indices. In the TFR, although the walls quench the flame and the post-flame gases, exhaust temperatures and residence time are non-negligible. The temperature dropped from about 685 ^{o}C to 500 ^{o}C in the upper third of the TFR, and TFR residence time in that region is on the order of one second. Therefore it is not possible to state conclusively that the observed results represent products which passed out of the flame in contrast to subsequent post-flame decomposition products.

An attempt was made to estimate the fraction remaining of a given compound using pseudo-first order rate constants and either the measured temperature of the thermocouple (TC) in the exhaust stack or the last unshielded TC in the upper third of the TFR. Since the overall stoichiometry was about 25 to 30% excess air and rate constants were expected to be higher for high O_2 than for low O_2 conditions, the UDRI $TSHiO_2$ constants were used for this purpose (Dellinger et al., 1984). The results of that calculation are shown in Table 7. Because PERC and TCE are predicted to be more difficult to destroy than TCB, reversed from the experimental observation, the first order decomposition kinetics model results would suggest that oxidative thermal decomposition was not the explanation for the observed results. It is possible that gasifying residues of oversize droplets caused non-stoichiometric conditions or that non-stoichiometric pockets of gas simply persisted in the upper reaches of the TFR (so that $TSLoO_2$ kinetics data should be used). In either case, TCB could be said to be more difficult to destroy in a flame environment than any of the other compounds tested.

The order of DE could also simply reflect differential compound volatility. The least volatile component of each

Table 5

Comparison of POHC DE with Various Ranking Methods

Compound	Relative Penetration	Drop	Rank based upon: Hc*	$TSHiO_2$*	$TSLoO_2$*	$TFMKLoO_2$
TCB	1.0E+00	1	4 (64/272)	3 (12/23)	1 (1/43)	1
PERC	6.0E-01	2	1 (11/272)	1 (2/23)	2	2
TCE	3.8E-01	3	3 (22/272)	2 (9/23)	3	3
TECA	7.6E-02	4	2 (16/272)	4 (21/23)*	4 (6/43)*	4
CP	9.3E-04	5	5 (NA)	NA (NA)	NA (NA)	5
HEPT	5.2E-04	6	6	NA	NA	6

* Values in parentheses are the ranks reported in the reference sources used except for 1,1,2,2-TECA for which it was assumed 1,1,1-trichloroethane would give similar ranking.

Hc - (CARB, 1986)
$TsHiO_2$ - (Dellinger, 1985b) observed T_{99}
$TsLoO_2$ - (Taylor, 1987)
$TFMKLoO_2$ - (Tsang and Shaub, 1982, 1987)

Table 6

Comparison of TCE:TCB:HEPT Penetration for Optimum and Oversize Droplets

	Penetration	
	Optimum	Oversize
TCE	6.2E-06	1.4E-04
TCB	8.8E-06	4.1E-03
HEPT	5.9E-08	2.6E-07

Table 7

Estimate of Fraction POHC Destroyed in Upper Third of TFR

	Residence time one second	
	Temperature - [K]	
Compound	958	773
trichloroethene	28%	3.4%
tetrachloroethene	8%	0.1%
1,2,4-trichlorobenzene	25%	0.2%
1,1,1-trichloroethane*	100%	16.1%

*Although 1,1,1-trichloroethane was not the POHC tested, it was felt that it would have similar characteristics to 1,1,2,2-tetrachloroethane (TCA), since molecular elimination of HCL was expected to be the lowest energy decomposition channel.

mixture pair was the most difficult to destroy compound in that mixture. Evidence from single droplet work at UC Davis has suggested that early extinction of the flame is facilitated if the highest boiling component in the droplet is a difficult to burn compound in contrast to a more readily burned fuel molecule, i.e., the higher boiling component tends to be more concentrated at the end of the droplet's lifetime (Sorbo et al., 1988). In any case, these data support the concept that TCB and PERC are difficult to destroy compounds, whether as a result of flame or non-flame processes.

The results of the oversize droplet DE study suggest that a relatively small number of chlorine atoms in comparison to the hydrogen atoms, 1:100 (5.3% Cl by weight), can produce noticeable effects on the combustion process as evidenced by the increased CO production (several hundred ppm above heptane alone - see Figure 8). This difference in CO production is believed to have resulted primarily from chemical effects since the reduced specific energy of the POHC/heptane mixtures resulted in overall exhaust temperature decreases of only 10 to 15 ^{o}C, while the change in theoretical adiabatic flame temperature, assuming the same amount of air supplied for the POHC/fuel mix as for fuel alone, was also only about 35 ^{o}C. The observed increase in CO is consistent with earlier observations of chlorinated mixtures burned in the TFR (Staley, 1985). In those experiments, introduction of large quantities of excess air was used to simulate a thermal "failure" condition (flame quenching). It should be noted that in full-scale incinerators, CO could subsequently be oxidized in the post-flame region, so that no apparent increase in CO emission would occur.

The results obtained from the current set of experiments contrast with similar earlier experiments (Kramlich et al., 1984). Large differences in penetration, i.e., greater than an order-of-magnitude, among the test compounds (acrylonitrile, benzene, chlorobenzene and chloroform) were not observed in the earlier oversize droplet study, although they would be expected based upon thermal decomposition data. The order of DE was also not that predicted by thermal decomposition kinetics; chloroform was observed to be the most difficult to destroy compound under several "failure" conditions. Furthermore, differences in compound Pt were only distinguishable when augmented by thermal quenching from the addition of large amounts of excess air, FTA > 1.5. In the present study, greater analytical sensitivity, achieved by use of a capillary column and a dual thermal desorption technique, allowed determination of differences in compound Pt near optimum stoichiometry, FTA of about 1.2 to 1.3. Large differences in compound Pt (or DE) were evident for TCB, TECA and CP. Resolution and identification of ROSEs in the current study also suggest that chloroform, benzene (BZ) and chlorobenzene (ClBZ) could be formed during the combustion process. This probably confounded the ranking of POHC DE in the earlier study. Given the further possibility of "sorption" on soot deposited on

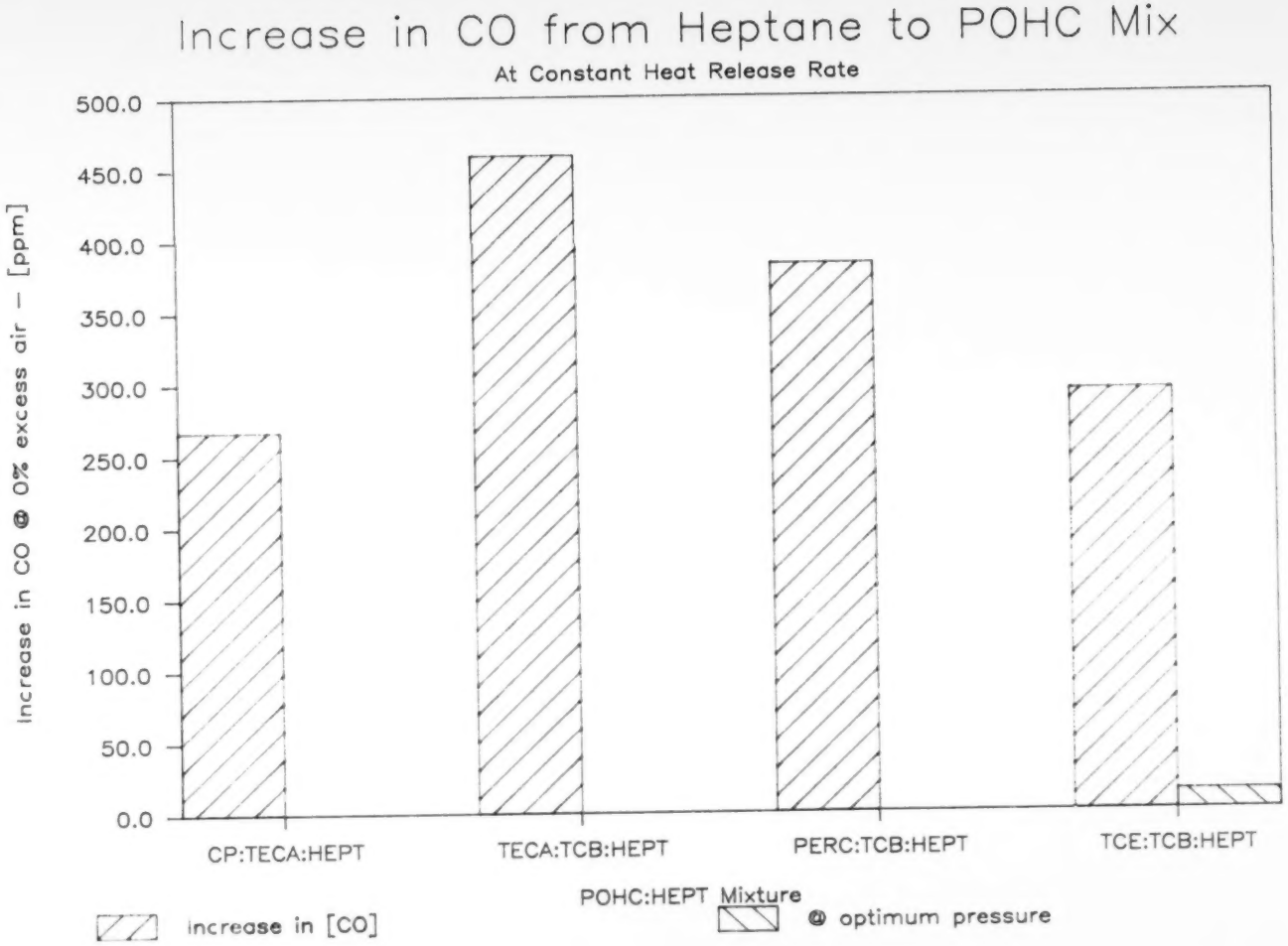

Figure 8. Increase of CO concentration at constant heat release rate for various mixtures under poor atomization. One comparison (TCE:TCB:HEPT) given for optimum nozzle atomization.

the cold walls of the TFR and release of low levels of ROSEs in subsequent tests (Mason, 1987), it should not come as a surprise that apparent consistency in DE was not observed under optimum combustion conditions in their study. Under "failure" conditions, differences in POHC DE became more apparent. For full-scale trial burns, the results of the current study simply confirm what has been suggested by others, i.e., that care should be exercised to select POHCs which are refractory, which are not readily formed in the combustion process, and which have been "spiked" into a waste in sufficient quantity to be easily quantified.

PRELIMINARY ASSESSMENT OF ROSEs

Identification of ROSEs was not the primary goal of the project. However, one of the last samples obtained from a TCE:TCB:HEPT experiment was subjected to GC/MS analysis as was one early test of the TAC tubes when burning a chloroform-heptane mixture. Using the retention time correlation constructed from those two analyses and simultaneous GC/FID analyses (see Figure 6 and Table 1), it was possible to use the GC/FID chromatograms from the remaining tests for tentative identification of peaks observed in the chromatograms. Retrospective analyses of the chromatograms were performed. The concentrations of selected PICs, tabulated as GC/FID area of the PIC normalized by area of the internal standard, is shown in Table 8. These data are discussed in the succeeding paragraphs.

When burning TECA-containing mixtures, a chromatographic peak assigned to TCE was clearly present. The ratio of TCE to TECA in those cases ranged from about 1.5 to 2.5. TCE concentrations were observed at levels about an order-of-magnitude lower when TCE was a POHC in the mixture and TECA was absent. The observation of TCE as a PIC of TECA was not surprising since the four-center elimination of HCl is believed to be the lowest energy decomposition pathway for TECA (Tsang, 1982). Staley (1985) also observed substantial quantities of TCE when burning TECA containing mixtures in the TFR. Thus formation of PICs that are specific to certain POHCs does appear to occur in the oversize droplet failure model.

On the other hand, benzene was observed in every POHC mix and in the heptane-only sample. Relatively large quantities were present whenever oversize droplets were formed (a factor of 10 to 30 times more than with optimum atomization).[2] Benzene was not a substantial component of the commercial technical grade heptane used. (It was not identified by GC/MS analysis of the fuel - see Table III-9 for a fuel analysis.) Clearly benzene was formed from one or more of the components of the fuel, possibly one of the cyclic alkanes present in abundance. Benzene is known to be formed from fuel molecules, even simple C_1 and C_2 hydrocarbons. In the oversize-POHC-mix-droplet tests, whenever substantial amounts of benzene were formed, a smaller peak corresponding to chlorobenzene was also observed, independent of the POHCs contained in the mixture. This was interpreted to mean that common recombination chemistry was probably occurring, e.g., substi-

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[2] Earlier it was noted that carbon tetrachloride (CCl_4) and benzene peaks eluted closely and that no attempt was made to distinguish between the two. The GC/MS data indicated that the vast majority of the co-eluting peaks' area could be attributed to benzene. Thus Table 8 and Figure 9 have been labelled to indicate that the sum of benzene (BZ) and carbon tetrachloride (CARB TET) is given, but most of the collected material is believed to have been benzene.

Table 8

Selected PIC Summary

GC/FID Relative Area Count

POHC Mix	DCM	CHCl3	EDC	BZ + CARB	TET	TCE	TOL	ClBZ
CP:TECA:HEPT	0.61	0.86	0.55	44.63	2.52	0.62	1.29	
TECA:TCB:HEPT	0.14	0.36	0.33	22.91	1.41	0.33	1.09	
PERC:TCB:HEPT	0.12	1.36	0.35	14.20	0.15	0.28	0.78	
TCE:TCB:HEPT	NA	NA	NA	21.29	0.33	NA	1.37	
HEPT*	0.04	0.67	0.44	3.26	0.04	0.17	N.D.	
TCE:TCB:HEPT*	0.05	0.87	0.42	2.68	0.02	0.26	N.D.	

*Optimum atomization pressure

Table 9

Fuel Constituents

Compound	Quantity	Retention time GC/MS
Freon 113	trace	---
methylhexane	14 to 15%	669
3-methylhexane	13%	693
1,3-dimethylcyclopentane	8%	708, 716
1,2-dimethylcyclopentane	5 to 7%	724
heptane (HEPT)	29%	765
methylcyclohexane	21%	818
ethylcyclopentane	trace	850
toluene (TOL)	4.5%	919

Approximately 98% of the total ion chromatogram was accounted for by the above compounds.

tution of a hydrogen atom on a ring by a chlorine atom, a bimolecular reaction which would be linearly dependent on benzene concentration. Benzene and chlorobenzene are commonly observed PICs in the field testing of full-scale units firing chlorinated wastes (Midwest Research Institute, 1986).

With the limited data available, concentrations of PICs were compared with CO concentrations. A surprisingly consistent relationship was observed for CO and benzene and is shown in Figure 9. The six points shown represent the four different POHC mixtures (higher values) and the two optimum atomization pressure test (lower values). These data were obtained over a period of two months, by different operators, Chang and Staley, and one of the points represents a GC/MS analysis corrected to give the corresponding relative FID response. Although fuel and air flowrates were matched as nearly as possible (to give the same heat release rate), and overall chemical composition was very similar, exhaust temperatures differed over about a 40 ^{o}C range. However, a monotonically decreasing relationship of exhaust temperature with CO was not observed (see Figure 10) as had been the case in an earlier study (Staley et al., 1986). This would seem to suggest that the residual levels of CO and benzene observed in the exhaust gases were related through a common physical mechanism, poor atomization, in conjunction with a common chemical mechanism, interference of CO oxidation by chlorinated species. Recall that CO levels exhibited definite increases when chlorinated compounds were burned in comparison to fuel alone under the same atomization condition (Figure 8). A speculative hypothesis would be that the common chemical mechanism is related to the availability of hydroxyl radicals to oxidize the CO and attack the benzene ring, rather than solely by temperature effects on rate constants. It is of particular interest to note that the POHC mixture that yielded the highest benzene level (CP:TECA:-HEPT) was not the most difficult to destroy, but rather, relatively the easiest! As will be discussed subsequently, experiments with single droplets suggest that a possible reason for this observation is related to the early four-centered elimination of HCl from CP and TECA, and the H-atom scavenging properties of HCl.

The remaining PICs in Table 8 could be placed into two groups, those which appeared to have some relationship to CO, and those whose concentrations appeared to be independent of CO levels. (See Figures 11 and 12, respectively.) Trichloroethene (TCE), chlorobenzene (ClBZ), toluene (TOL) and dichloromethane (DCM), concentrations appeared to vary directly with CO concentration, whereas trichloromethane ($CHCl_3$) and dichloroethane (EDC) appeared to be somewhat independent of CO concentration. The latter four compounds' concentrations were quite low, so that they might simply represent a low-level background present because of gradual release from previous deposits of soot adhering to the cold walls of the TFR. The data are limited, however, so

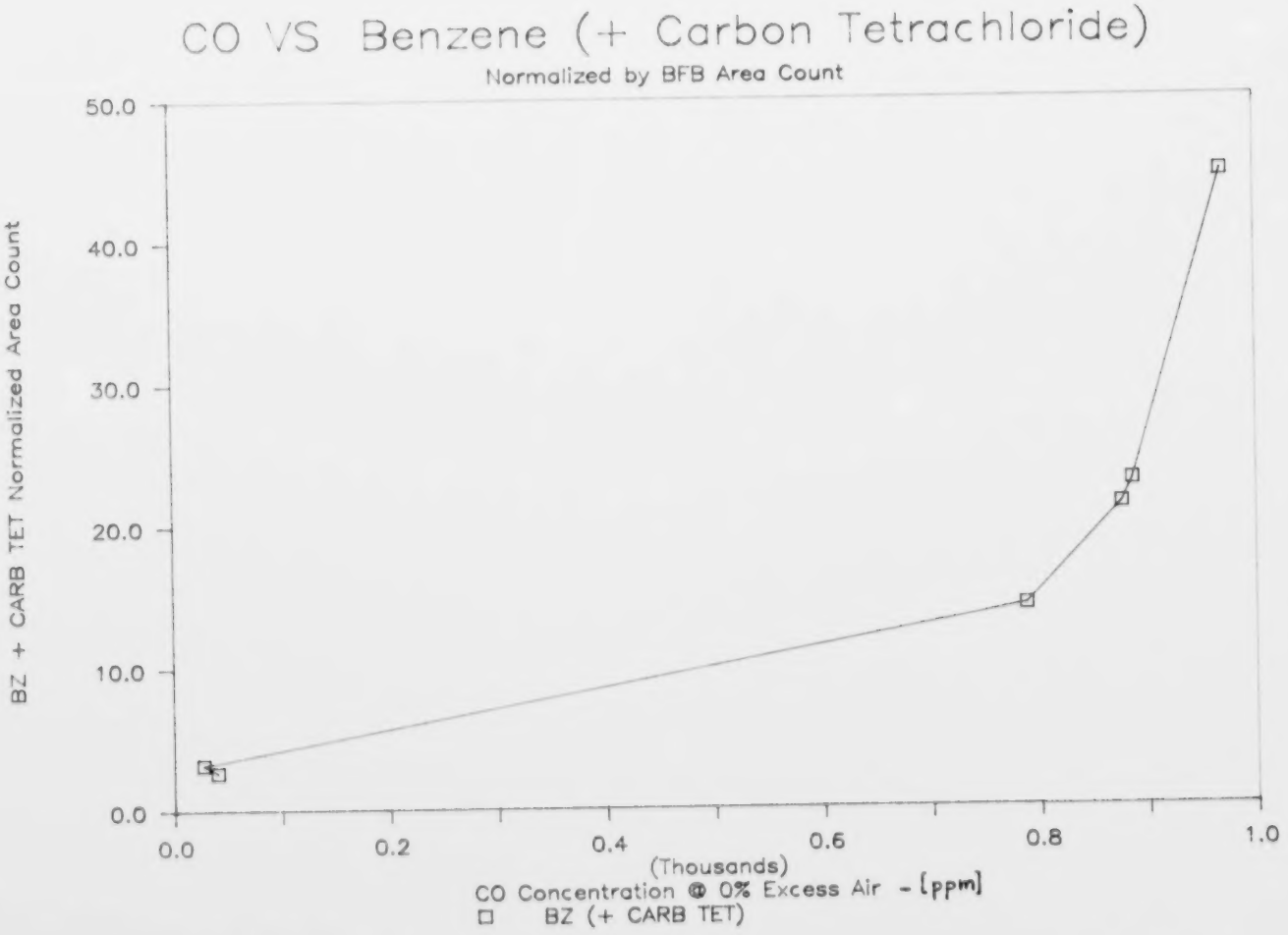

Figure 9. Exhaust CO concentration versus sum of benzene and carbon tetrachloride concentration. Carbon tetrachloride is believed to be a small or negligible portion of total FID area count.

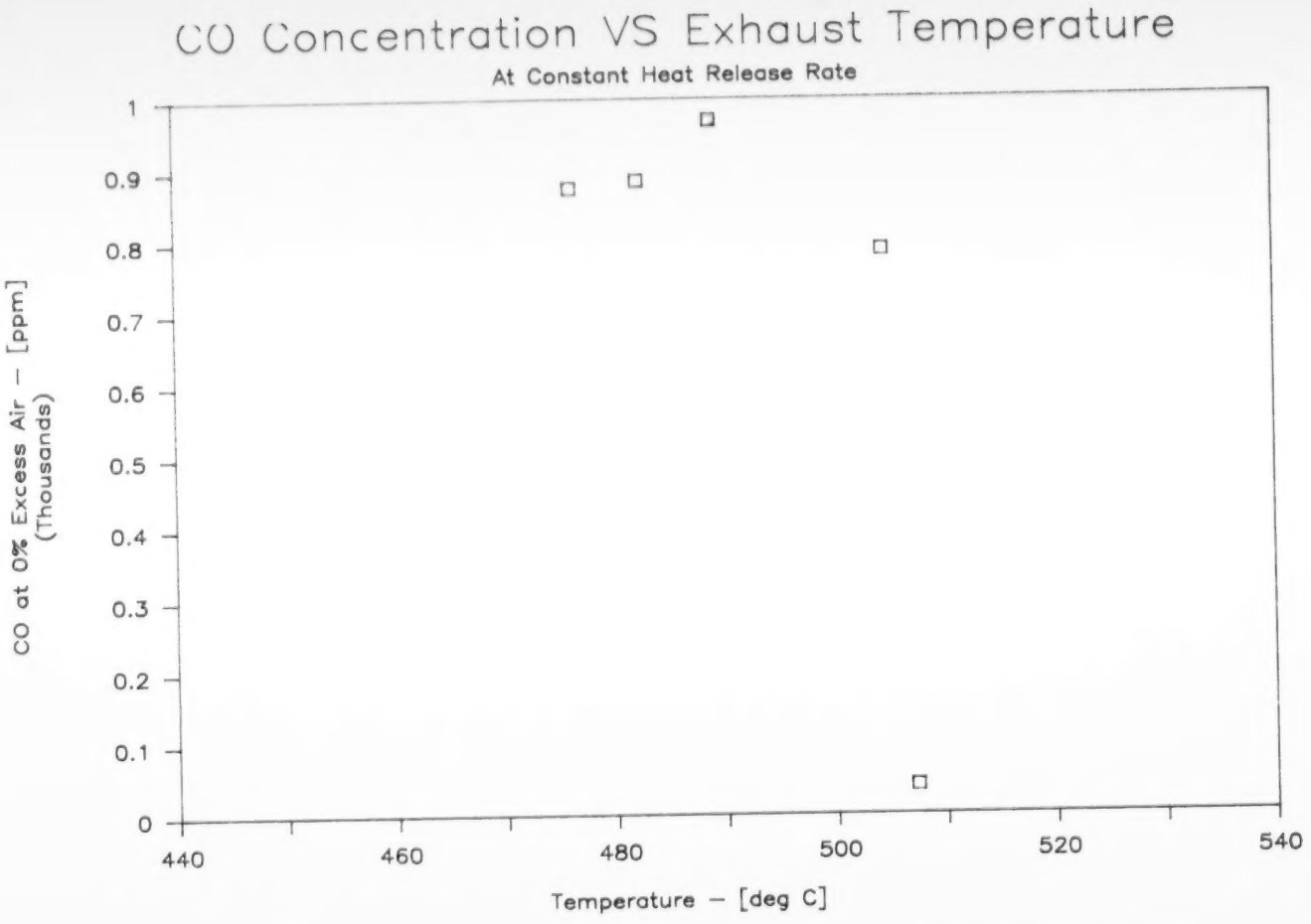

Figure 10. Exhaust CO concentration versus exhaust temperature.

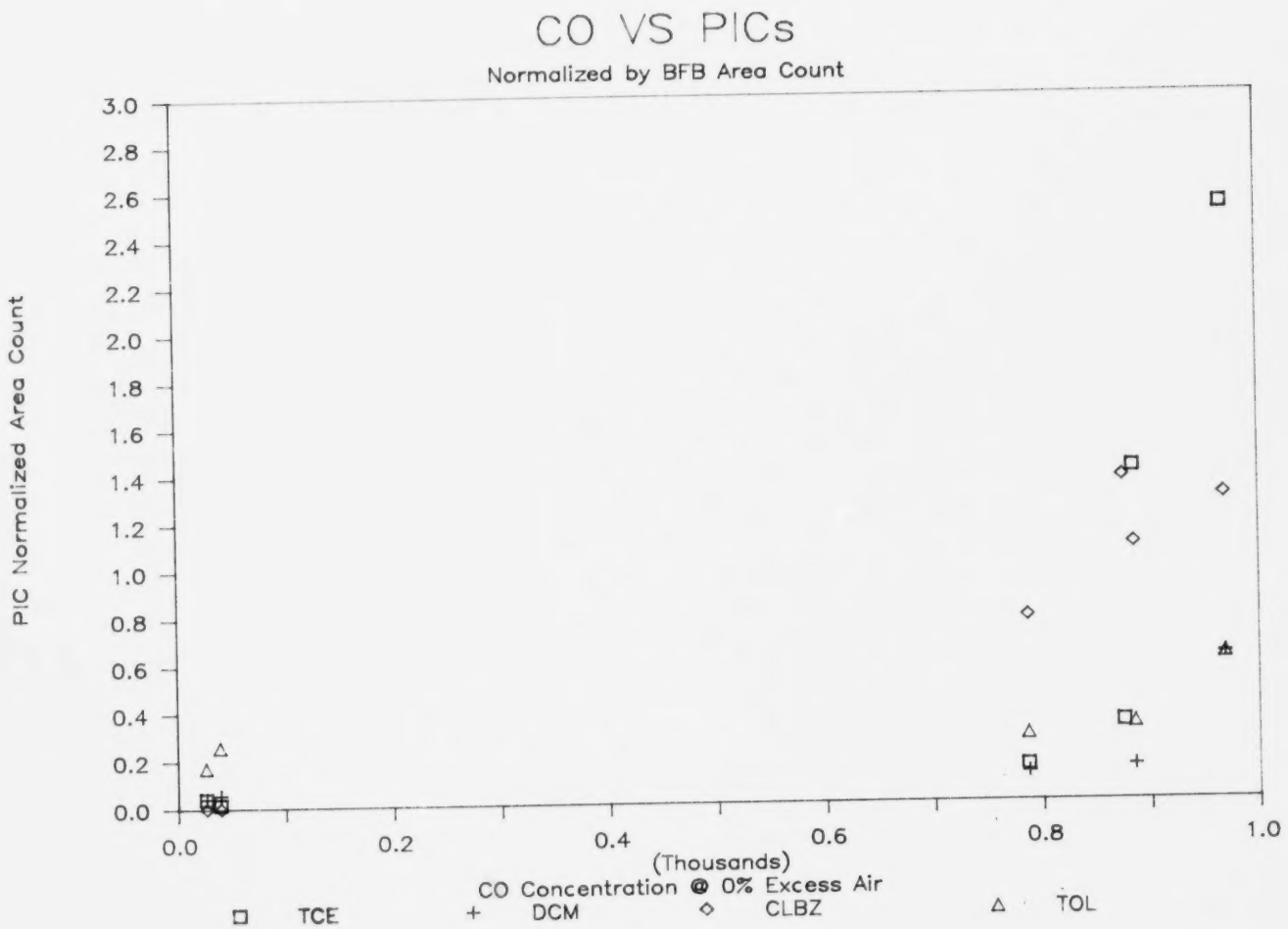

Figure 11. CO concentration versus PICs that appeared to vary directly with CO concentration.

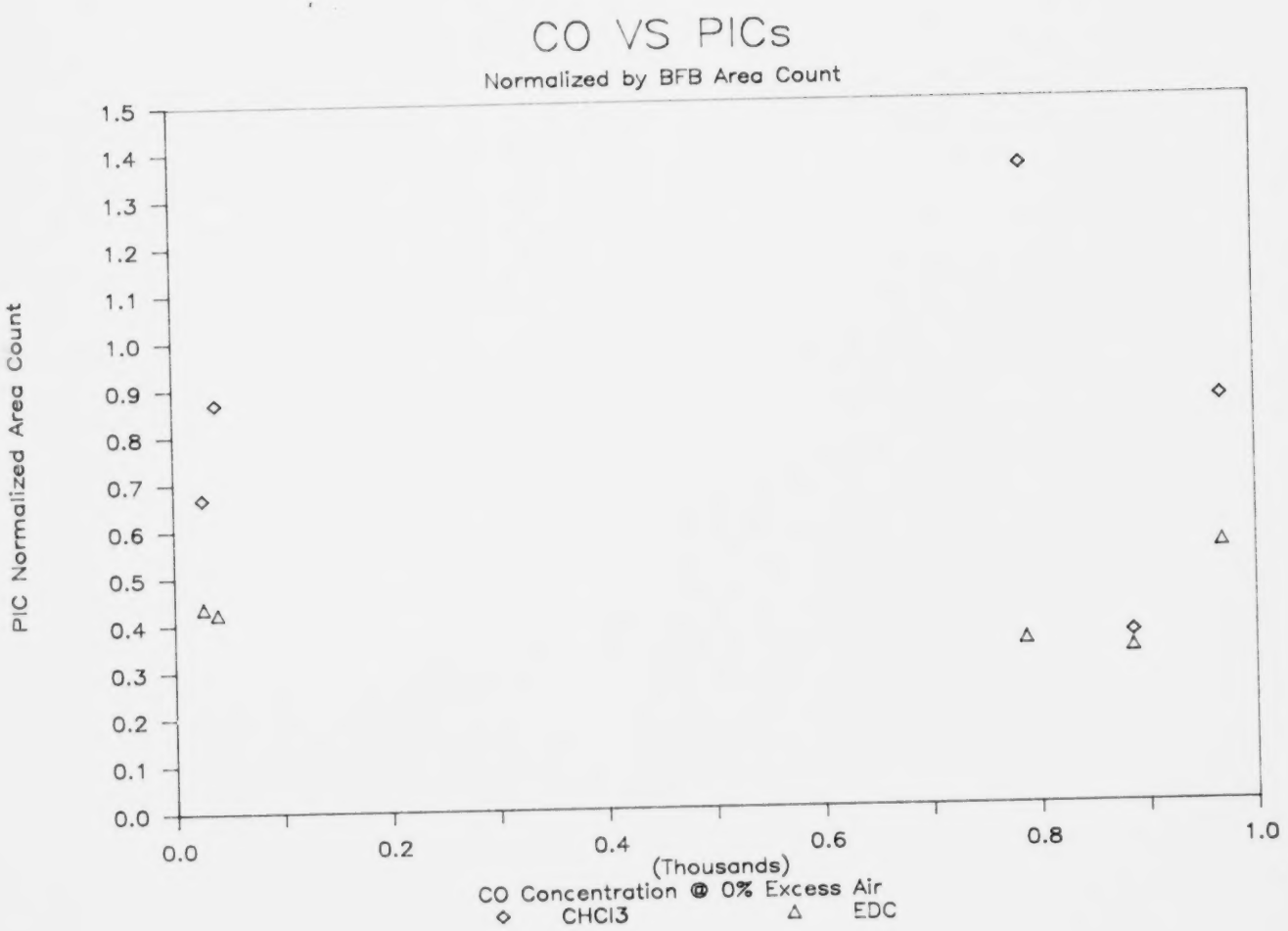

Figure 12. CO concentration versus PICs that did not appear to vary with CO concentration.

too great a significance should not be attached to this observation.

RELATIONSHIP TO UCD DROPLET EXPERIMENTS

An original goal of this project was the determination of the relationship between observations of isolated droplet burning and the combustion of droplets in sprays. Isolated droplet burning experiments were being conducted concurrently at UC Davis (UCD) by Mr. Nelson Sorbo, under the guidance of Professor C.K. Law of the Department of Mechanical Engineering. The most relevant of the droplet-burning results has been summarized in this section of the report. Additional details of those experiments are contained in a report to the California Air Resources Board (CARB) by Sorbo et al., (1988).

Basically, data on burning-rate (rate of change of droplet diameter squared with time), extinction diameter (the diameter of the droplet at which an exothermic reaction in the region surrounding the droplet spontaneously ceases - often, but not always, corresponding to the end of a visible flame), and droplet liquid-phase composition were measured. The following compounds were studied at UCD in common with those at CHL: chloropentane (CP), 1,1,2,2-tetrachloroethane (TECA), tetrachloroethene (PERC), and 1,2,4-trichlorobenzene (TCB). Trichloroethene (TCE) was not among the compounds for which reliable data were available because of difficulties in generating stable droplets of compounds having boiling points less than about 90 ^{o}C. Similarly, chlorodecane (CD), which was studied at UCD, was not studied at CHL because of difficulties with its quantitation on the analytical chromatographic column in use at CHL.

A significant UCD result related to observed differences between mixtures of TECA/nonane (B.P. = 146 ^{o}C & 151 ^{o}C, respectively) and PERC/octane (B.P. = 121 ^{o}C & B.P. = 125 ^{o}C, respectively). The TECA/nonane and PERC/octane mixtures were chosen to minimize differences in component volatility, so that a droplet's composition would remain approximately constant throughout its lifetime. Burning-rate constants, K, are plotted in Figures 13 & 14 as a function of the volume % of the CHC in the mixture. Qualitatively the two curves are similar, however important differences exist. In particular, the Cl:H ratio at which burning-rate decreases sharply to that of pure vaporization (no burning), occurred at about 0.8 for TECA/nonane, while it was about 3.0 for PERC/octane. This was totally unexpected. Other measures of "incinerability" such as gas phase thermal stability, or heat of combustion predict that PERC should be more difficult to destroy than TECA. Therefore, one might naively suppose greater difficulty in sustaining the flame with the less readily decomposed species, which in this case also had a lower heating value, i.e., PERC. Furthermore we had anticipated that at Cl:H ratios greater than about 1.0, there would be sufficient Cl

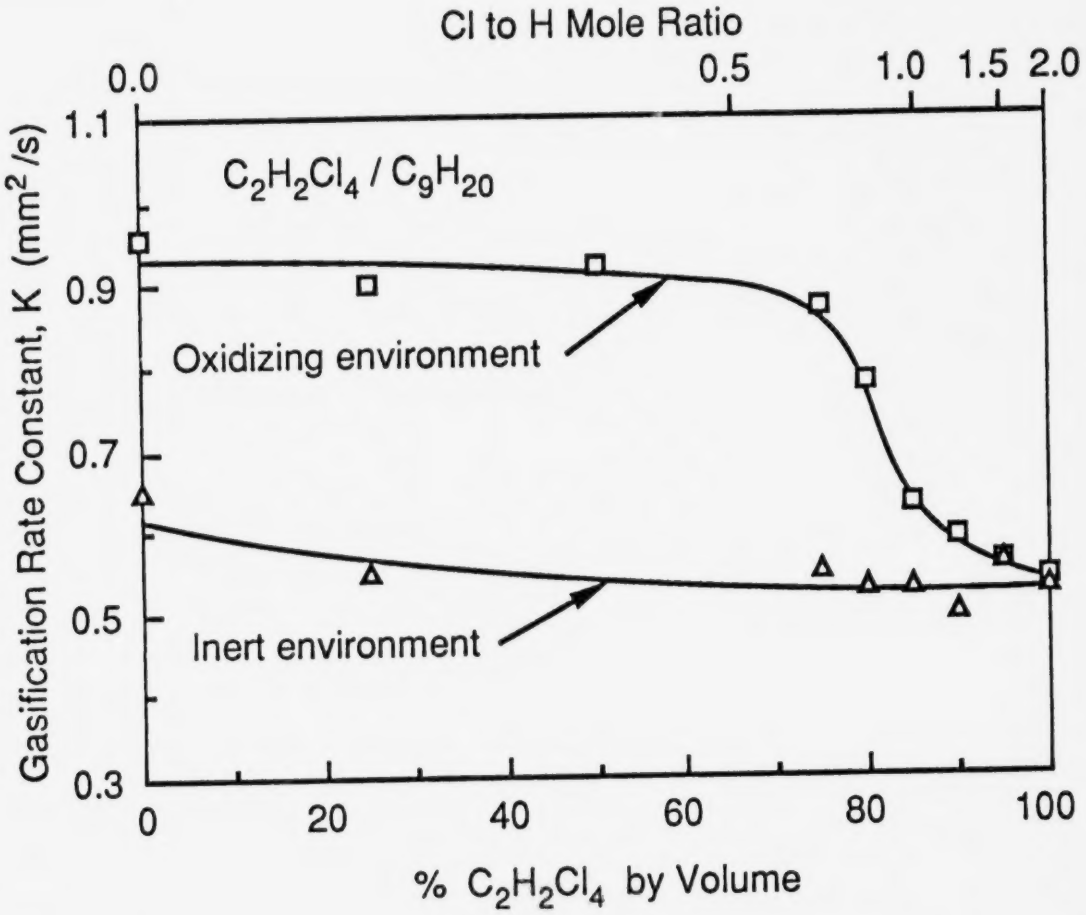

Figure 13. Gasification rate constants of tetrachloroethane/nonane droplet mixtures in oxidizing and inert environments.

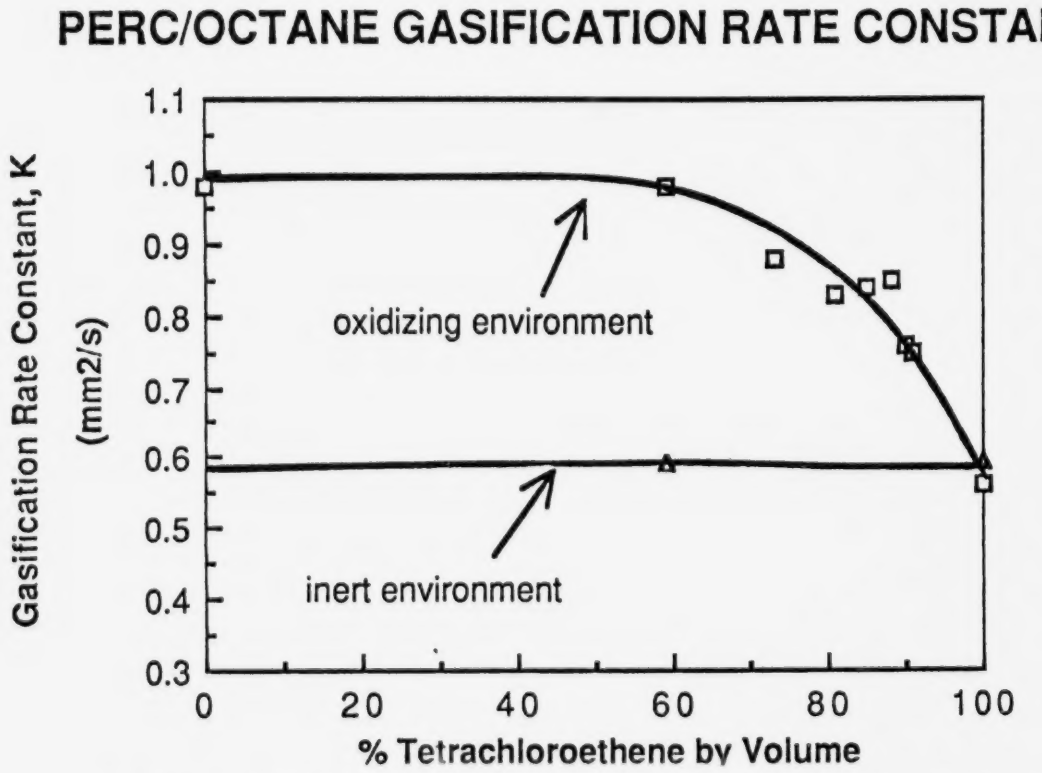

Figure 14. Gasification rate constants of tetrachloroethane/octane droplet mixtures in oxidizing and inert environments.

species liberated to deplete a key species in the chain of reactions in the combustion of hydrocarbons, namely H atom. With the PERC/octane mixture this ratio was greatly exceeded. A hypothetical, and somewhat speculative explanation for the observation is given below.

First, it should be noted that there is no evidence that the fraction of the TECA which vaporized and passed through the flamelet surrounding the drop was not destroyed to a greater degree than the PERC. In fact, it is our opinion that the degree of destruction of TECA was probably greater than that of PERC while the flamelet was present. However, when the flamelet extinguished at larger Cl:H ratios, for both the TECA/nonane and PERC/octane mixtures, it occurred at significantly larger extinction diameters, about 140 μm compared to less than 40 μm, respectively. Thus the fraction of the original droplet in the liquid phase which remained unburned at flame extinction was greater for both the TECA/nonane and PERC/octane mixtures.

The extinction of TECA/nonane flamelets at a relatively low Cl:H ratio can be explained by the thermal decomposition characteristics of TECA. Chloroalkanes having hydrogen and chlorine atoms on adjacent carbons are subject to concerted four-center elimination of HCl (Tsang and Shaub, 1982). In the TFR, TCE, the product of the HCl elimination reaction from TECA, has been the most prevalent PIC observed when burning TECA (Staley et al., 1986; this study). The gases and vapors on the fuel-side of the diffusion flame surrounding the droplet, range from the flame temperature (at the flame) to about the boiling point of the mixture (at the drop surface). Thermal decomposition studies at UDRI suggest that TECA decomposition would begin in the range of about 600 ^{o}C or lower (Dellinger et al., 1984; Taylor and Dellinger, 1986; Taylor and Dellinger, 1987). Observation of a visible emission from droplets of pure TECA (non-burning) have been made at that temperature (Sorbo et al., 1988). Thus it is hypothesized that the four-center elimination reaction is sufficiently rapid to liberate HCl in advance of the flame. Senkan (1982) has surmised that H-atom scavenging by HCl,

$$H + HCl \text{ -----> } H_2 + Cl,$$

can be a significant scavenging reaction, and has presented rate data (Senkan, 1984) indicating that the reaction proceeds at a rapid rate in the temperature range described above. The Cl-atom liberated by the above reaction can further react with H atoms

$$H + Cl \text{ -----> } HCl.$$

Furthermore, the four-center elimination reaction is endothermic by about 13 kcal/mole. All of these factors contribute to a reduced rate of reaction. According to flame extinction theory (Law, 1975), as the droplets decrease in size, the Damkohler number (ratio of characteristic time for mass flow to charac-

teristic time for chemical reaction) tends to zero. What this means in effect is that there is insufficient time in the "flame" for the oxidation reactions to be completed. As a result, the full heat of combustion is not released and some of the reactant "leaks" through the flame. The reduction in heat energy leads to a corresponding reduction in flame temperature and a further slowing of reaction rates. Because of the exponential dependence of key reaction rates on inverse temperature, a critical Damkohler number exists at which the flame spontaneously extinguishes. The effect of the early release of radical scavenging species and the endothermicity associated with the HCl elimination reaction act to slow reaction rates, leading to a larger extinction diameter at which the critical Damkohler number is reached.

The above hypothesis is also consistent with two other observations in the TFR. There was a general tendency for CO to increase with the addition of chlorinated POHCs, but the highest absolute concentrations of CO and benzene occurred for the CP/TECA/HEPT mixture, i.e., the case for which the POHC DE was greatest. Benzene and CO are both known to be difficult to oxidize without the presence of hydroxyl radical. Hydroxyl radical concentration is in turn dependent upon an adequate supply of H-atoms. Again, this observation does not provide conclusive evidence by itself, but is suggestive.

Early in the development of the TFR by EERC, studies were conducted of POHC incinerability, burning mixtures which contained chloroform (Kramlich, 1984). In those studies chloroform was found to be more difficult to destroy than chlorobenzene, benzene, and acrylonitrile under several burning conditions including simulated nozzle atomization failure, quenching with excess air, or quenching with cooled coils. Those results seemed anomalous in light of subsequent work in the TFR with other compounds and the relative ease of thermal decomposition of chloroform. It was suspected that the primary reason for the presence of chloroform was formation or re-formation of chloroform as a PIC. However, recent UDRI studies on chloroform suggest that there is a low energy HCl elimination pathway for this chloroalkane species as well (Taylor, 1986a)

$$CHCl_3 \text{ -----> } :CH_2 + HCl.$$

If that is true, then at least a portion of the chloroform remaining in the EERC tests could have been the result of chlorine species (HCl, Cl, Cl_2) accelerating normal flame extinction processes. Alternatively, $CHCl_3$ has a relatively high volatility (B.P. = 61 ^{o}C) and could have impeded flame ignition processes. Volatility effects are discussed further below

A second finding of the UCD study relates to the effect of volatility differences between a POHC and a HC fuel. Figure 15 illustrates droplet composition as a function of scaled droplet

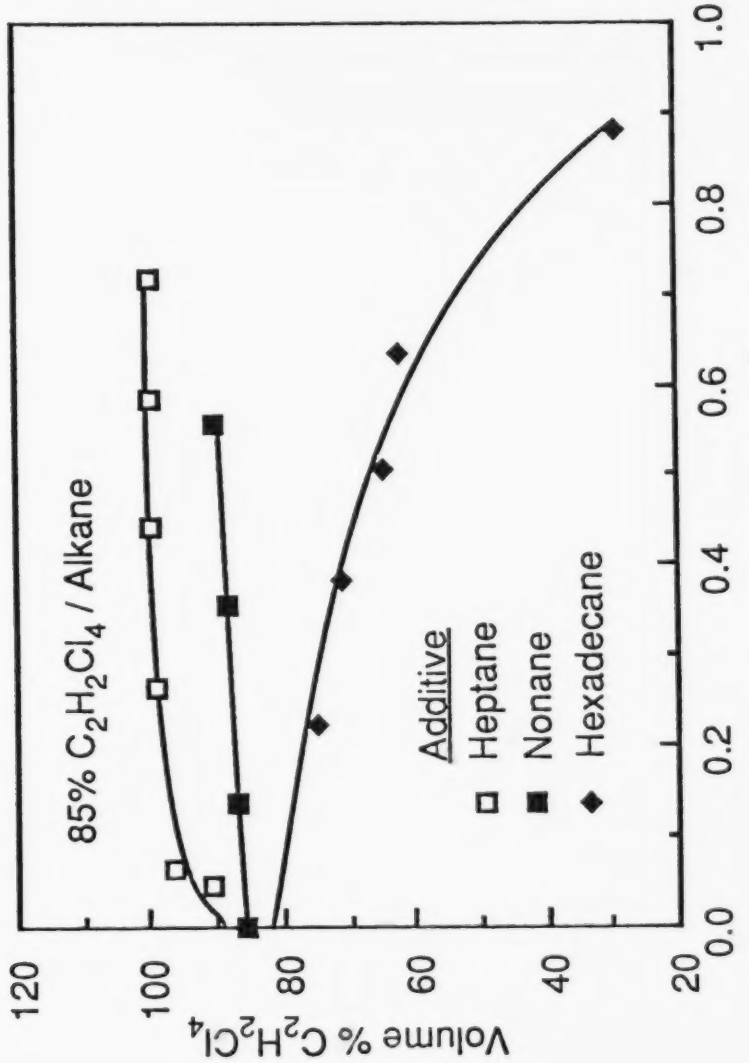

Figure 15. Sampling history of droplets of 85% tetrachloroethane (by volume) in alkanes in oxidizing environments.

diameter squared (effectively the fraction of a droplet's lifetime) for TECA/HC mixtures initially 85% by volume TECA. When TECA was mixed with heptane, the heptane was driven out of the droplet early in its lifetime. When mixed with nonane, a compound with nearly identical boiling point, the droplet composition remained essentially unchanged throughout the droplet lifetime. When mixed with a less volatile species, hexadecane, the TECA concentration in the droplet gradually decreased. Concurrent observations of burning-rates of the mixtures indicated that extinction of the heptane mixture occurred earlier than for the hexadecane mixture. Interestingly, in the TFR tests, the boiling points of each CHC tested was greater than that of the technical grade heptane (which consisted of a range of compounds boiling near 100 ^{o}C). TCB, which had the lowest DE, also had the highest boiling point of the compounds studied.

Volatility differences may be of practical significance in determining strategies for blending of waste and fuel. A "heavier" fuel oil (up to a point) might actually promote more complete burning of any CHCs before the flame extinguishes. A mixture of lower and higher boiling fuel components compared to the CHCs, might be even better as both ignition and extinction properties of the mixture would be improved (Sorbo et al., 1988a). Volatility differential effects also have been shown to promote "secondary atomization", but only at relatively higher concentrations (10% or more) of the volatile component (Kramlich, 1986).

CONCLUSIONS

Few definitive conclusions can be drawn from a limited set of data. However, the following tentative statements can be made on the basis of the experiments presented in this report:

1) The oversize-droplet model, in the TFR, provides a consistent picture of incomplete combustion of large fuel/POHC droplets. Flame-extinction phenomena observed in single droplet combustion experiments and the "rogue droplet" hypothesis are consistent with the observations. The observations made during this study do not establish that they are the correct explanation for the observed results, since direct droplet collision with the cold walls of the TFR cannot be ruled out and sufficient temperature and residence time existed for some thermal decomposition to occur.

2) The destruction efficiency of five POHCs was established with the oversize-droplet model. The resulting ranking agreed with both gas-phase thermal stability and theoretical flame-mode kinetics rankings under low oxygen conditions. This was true even though an overall fuel-lean stoichiometry prevailed in the combustion unit under conditions of moderate turbulent mixing. The order of difficulty of destruction was TCB > PERC > TCE > TECA > CP > HEPT.

3) Given close attention to reproducing combustion conditions as nearly as possible, increases in CO level were apparent when simulating a "failure condition" given relatively small additions of chlorine into a hydrocarbon fuel.

4) Evidence was obtained for a relationship between CO and benzene emissions for the specific failure condition of oversize-droplets combined with flame-quenching at optimum stoichiometry. A few other PICs, trichloroethene, chlorobenzene and possibly toluene and dichloromethane also appeared to increase with increasing CO emissions under the above conditions.

5) Although the CP/TECA/HEPT mixture exhibited the highest DE of the two POHCs in the mixture, it also yielded the highest levels of the PIC benzene under conditions of constant heat release rate and overall stoichiometry. This was interpreted as evidence of chlorine species interference with chain branching reactions needed to produce OH radicals.

6) Evidence for POHC-specific and POHC-independent formation of PICs was obtained. TCE produced from TECA

was an example of the former, and ClBZ was an example of the latter.

7) Experiments conducted at UCD on effects of volatility on droplet composition indicate that the assumption of constant DE of POHCs exiting the flame zone will not hold in general. Unfortunately, there does not appear to be any simple method for ranking flame destruction efficiency, in a general way, using droplet burning characteristics.

A hypothetical explanation for the observed relationship between CO and benzene was offered. The gist of the hypothesis is that the four-centered molecular elimination of HCl from the chloroalkanes studied, occurred on the fuel side of the diffusion-flame surrounding droplets. The elimination reaction can retard chemical reaction rate by either of two means, endothermicity of the reaction or H-atom scavenging by the HCl molecule liberated. In either case, OH radical concentrations are reduced, and the droplet diameter at which the critical Damkohler number is attained becomes larger, leading to larger flame extinction diameter.

A number of additional lines of research are suggested for the future. First, the ability of chloroalkanes (and bromoalkanes) to increase flame extinction diameter, in general, should be examined in both spray and droplet experiments. Second the effects of fuel additive volatility on the completeness of droplet burnout should be examined in sprays to determine whether the single droplet predictions for improved DE can be obtained in sprays. Third, sampling of ROSEs at the point of droplet extinction should eliminate the possibility of thermal decomposition. Thus definitive evidence regarding the relative importance of flame extinction phenomena in determining the order of incinerability of POHCs could be obtained.

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